

Response to the comments on the paper by Referee #2

Main text:

On the one hand the authors use model results of 3D-calculations and on the other hand they employ measured concentrations of these species. Deviations from unity are a hint to non-equilibrium conditions or to other reasons such as incorrect reaction rates, erroneous model calculations or errors in the retrieved data. The fundamental idea was to derive such expression not depending on water vapor. The interpretation of deviations from unity is certainly complicated. What means for instance -1% deviation or $F(\text{OH}, \text{HO}_2, \text{O}_3)=0.99$? It indicates that, generally speaking, the agreement is quite good. But in case of stronger deviations it is difficult to say, what is the reason for this discrepancy?

In the revised manuscript (see Fig. 3 and lines 251-262), we have directly compared the source of OH ($P_{\text{OH}}^{\text{H}_2\text{O}}$) due to the reactions $\text{H}_2\text{O}+h\nu \rightarrow \text{H}+\text{OH}$ и $\text{O}({}^1\text{D})+\text{H}_2\text{O} \rightarrow 2\text{OH}$ with the main source of that component, P_{OH} , via the reactions $\text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2$, $\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$ and $\text{H} + \text{HO}_2 \rightarrow 2\text{OH}$. It can be seen from Fig. 1 and Fig. 3 that the indicated 3–4 % deviation of $\langle F \rangle$ from 1 in the region between 76 km and 86 km is largely due to the neglect of the reactions $\text{H}_2\text{O}+h\nu \rightarrow \text{H}+\text{OH}$ и $\text{O}({}^1\text{D})+\text{H}_2\text{O} \rightarrow 2\text{OH}$.

Also, one should note the following. We found the mistake in Fig. 1 below 50 km caused by the use of improper computer number format (float32 instead of float64). The value of $\langle F \rangle$ below 50 km increases.

Minor comments:

The paper has a very voluminous introduction of about 39% related to the entire paper. It has the character of a review paper. I will it not criticize that, but I will it only mention here.

Indeed, the Introduction contains elements of the review. Thus, we wanted to show that the proposed method of evaluation of simultaneous measurements of mesospheric components has a wide range of possible applications for other areas of the atmosphere.

Line 165: 150 km is already the middle thermosphere.

Corrected. See line 166.

Line 174: entered, maybe better mentioned

Corrected. See line 197.

Line 178: H=7 km is an approximated mean scale height. (1 km scale height corresponds to about 33 K or 7 km to 231 K mean temperature)

Corrected (see lines 197-202 and Figs 1-3). In the revised manuscript, the pseudo-height scale was replaced by pressure levels. In addition, we indicated the approximate heights in km calculated from the pressure profiles for a given month utilizing averaged temperature profiles of the model and hydrostatic equilibrium.

Line 194: reaction rate constants; according to? Quotation?

Corrected. See line 227 and Table 1.

Line 198: The net production term of hydrogen radicals is in essential JH2O[H2O]. Why do you neglect this term in (10)? Too small compared with the other terms in equation (10) and consequently the approach do not depend on water vapor?

In the revised manuscript, we have directly compared the source of OH ($P_{OH}^{H_2O}$) due to the reactions $H_2O+h\nu \rightarrow H+OH$ and $O(^1D)+H_2O \rightarrow 2OH$ with the main source of that component, P_{OH} , via the reactions $HO_2 + O \rightarrow OH + O_2$, $H + O_3 \rightarrow OH + O_2$ and $H + HO_2 \rightarrow 2OH$. The ratio $P_{OH}^{H_2O} / P_{OH}$ does not exceed 3-4%.

Two corrections are made in the revised manuscript:

- (1) a new figure is added (Fig. 2-3);
- (2) the following text is inserted (lines 251-262):

«Note also that Eq. (1) and Eq. (6) take into account only the main daytime source of OH (P_{OH}) specified by reactions R18, R14, and R21:

$$P_{OH}=k_{18} \cdot HO_2 \cdot O + 2k_{14} \cdot HO_2 \cdot H + k_{21} \cdot O_3 \cdot H$$

These reactions run “inside” the HOx (H, OH, HO₂, H₂O₂) family and do not perturb its total concentration. The height–latitude cross-sections of $\langle P_{OH} \rangle$ for each month are presented in Fig. 2.

The next important daytime source of OH is specified by reactions R59 and R7 involving H₂O, the main source for the HO_x family:

$$P_{OH}^{H_2O} = (k_{59} + 2 \cdot k_7 \cdot O(^1D)) \cdot H_2O$$

Figure 3 shows height–latitude cross-sections of $\langle P_{OH}^{H_2O} / P_{OH} \rangle$ for each month. Comparing Fig. 1 and Fig. 3, we conclude that the previously indicated 3–4 % deviation of $\langle F \rangle$ from 1 in the region between 76 km and 86 km is largely due to the neglect of these reactions.»

Line 202: ...of ozone ()?

Corrected. See line 230.

Line 204: The aim is to eliminate O and H and to derive an expression only depending on OH, HO₂, O₃.

Done. We added new sentence (see line 228):

«We eliminate O and H from Eqs. (1)-(3) and derive an expression depending only on OH, HO₂, O₃.»

Line 211: α =(...) could be equation (14.2) and (14) then (14.1) or (15) and the following equations (x+1). There is a large step from equation (10) – (13) to equation (14). Could you give some intermediate steps?

Done. The Sec.2 was rewritten. All the steps needed to derive the equation $F(OH, HO_2, O_3) = 1$ were presented. It should be noted that the reaction $OH + HO_2 \rightarrow H_2O + O_2$ was removed from the analysis. Our numerical calculations showed that its contribution to the analytic expression $F(OH, HO_2, O_3) = 1$ is less than 1%.

Line 218: k_2 decreases strongly below the lower mesosphere and stratopause. Ozone is no longer in photochemical equilibrium there.

We cannot fully agree with the comment. In particular, daytime lifetime of O₃ in the altitude range of 30-50 km varies in the range 100-1000 s (Brasseur and Solomon, 2005). So, O₃ can stay in photochemical equilibrium depending on height and duration of daylight.

The following sentences were inserted in the revised manuscript (see lines 247-250):

„Note that these components remain short-lived below 50 km (with the lifetimes of about 10²-10³ s (Brasseur and Solomon, 2005)) depending on height and duration of daylight. However, for quantitative description of their daytime equilibrium it is

necessary to include additional reactions involving, in particular, the components of the NO_x family.”

Line 234:…certain altitude z…

Corrected. See line 290.

Line: 239: Factor $\sigma_j \sqrt{2\pi}$?

Corrected. See line 295.

Line 296:…fall into one…

Corrected. See line 360.

Line 304-318: In the lower thermosphere the system is not in chemical equilibrium. Transports play a significant role (see also Grygalashvyly et al. 2012).

Section 6: The characteristic time of atomic oxygen is about $\tau_O = (k_1 \cdot O_2 \cdot M)^{-1}$. At 90km is $O_2 = 1.47 \times 10^{13} \text{ cm}^{-3}$, $M = 7 \times 10^{13} \text{ cm}^{-3}$, and $k_1 \approx 10^{-33} \text{ cm}^6 \text{ s}^{-1}$ depending on temperature. The characteristic time has then an order of 10^6 s. About one order smaller is the characteristic time of H, but still large. Both the production and the loss term of HO₂ depend on H and O being not in photochemical equilibrium in the lower thermosphere. Therefore a discrepancy relating to HO₂ one should expect.

Here, apparently, there was a misunderstanding caused by a possibly insufficiently clear indication in the manuscript. In these parts (Lines 304-318 (new 368-383), Section 6) we consider lower and middle mesosphere, heights below 0.01 mbar (~78km). In the revised manuscript, the upper height is 0.046 mbar (~71-72 km).